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**FABRICATION OF 3-D PHOTONIC BAND GAP CRYSTALS VIA
COLLOIDAL SELF-ASSEMBLY**

Prepared By:	Girija Subramaniam & Shannon Blank
Academic Rank:	Professor (GS), Student (SB)
Department:	Chemistry
Institution:	Penn State University
NASA/MSFC Directorate:	Science
MSFC Colleague:	Andrew Keys

Introduction

The behavior of photons in a Photonic Crystals, PCs, is like that of electrons in a semiconductor in that, it prohibits light propagation over a band of frequencies, called Photonic Band Gap, PBG [1-5]. Photons cannot exist in these band gaps like the forbidden bands of electrons. Thus, PCs lend themselves as potential candidates for devices based on the gap phenomenon. The popular research on PCs stem from their ability to confine light with minimal losses. Large scale 3-D PCs with a PBG in the visible or near infra red region will make optical transistors and sharp bent optical fibers. Efforts are directed to use PCs for information processing and it is not long before we can have optical integrated circuits in the place of electronic ones.

Fabrication of PCs via Self-Assembly

Many methods have been utilized to prepare PCs. Nanomachining [6], lithography [7] and 3-D holography [8, 9] are a few of the most commonly used but they suffer from being involved, complex, and expensive. These drawbacks also include the inability to produce uniform submicron ordering over large area. Self-assembly of colloidal silica spheres leads to opaline crystals with Face Centered Cubic (FCC) close packing.

Calculations and experiments show that these opal structures do not have a complete photonic band. However the inverse structures i.e. air spheres in high refractive index background dielectric material have a complete photonic band gap [10-12]. The goal of this project is to make the metallic inverse opal structure, a PBGM with complete gap. Tungsten inverse opals are of special importance because of their ability to modify thermal radiation [13-19]

The strategies to inverse opals involve the following steps:

Synthesis of Monodisperse silica spheres

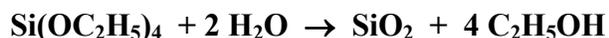
Self-assembly in Face Centered Cubic (FCC) packing to form the opal template

Infiltration of the interstitial air gaps with materials of interest

Removal of the template to form the inverse opal structure

Synthesis of Silica Spheres

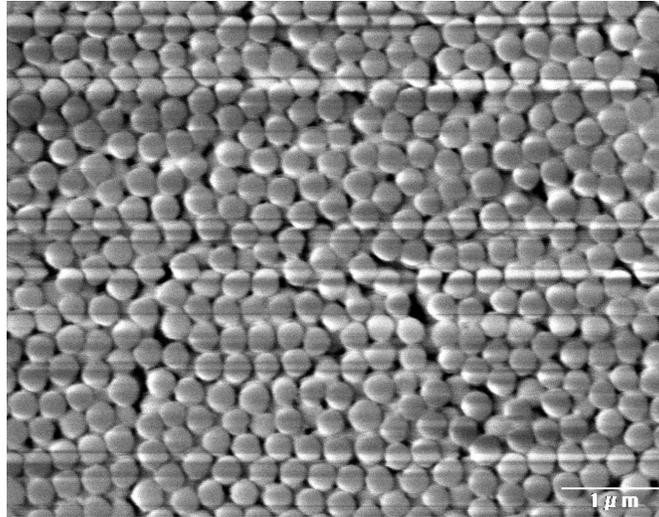
Highly monodisperse silica particles can be obtained by Stober's process [20]. It involves the hydrolysis of tetraethyl orthosilicate, catalyzed by ammonia in aqueous ethanol. Spheres with a diameter of 480nm were prepared successfully with very high monodispersity (reference 2003 report).



To prepare larger silica particles greater than 1 μm , Giesche's continuous growth process [21, 22] was adapted. In the continuous growth process, reactants are added at a constant rate to a "seed," which is a suspension of smaller silica particles. During our trial, the rate of addition was increased many fold for lack of peristaltic pumps. To our surprise, absolutely no growth occurred

using the seed spheres of 1.4 μ m, instead the reactants mixed producing 280nm spheres (Figure 1).

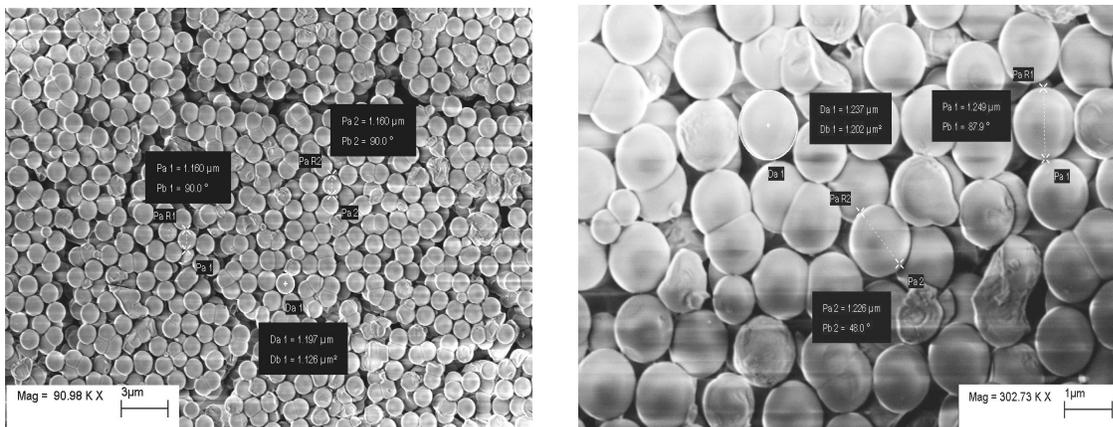
Figure 1: SEM Image of 280nm Spheres



Purification

Purification was done to decrease the polydispersity of the spheres by repeated wash with ethanol centrifugation. Monodispersity was checked using a Zetapal Size Analyzer and SEM measurements. SEM pictures clearly show that the bigger spheres (\sim 1.4 μ m) were highly polydispersed (Figure 2) in spite of purification.

Figure 2: SEM Images of Polydispersed 1.4 and 1.2 μ m Spheres



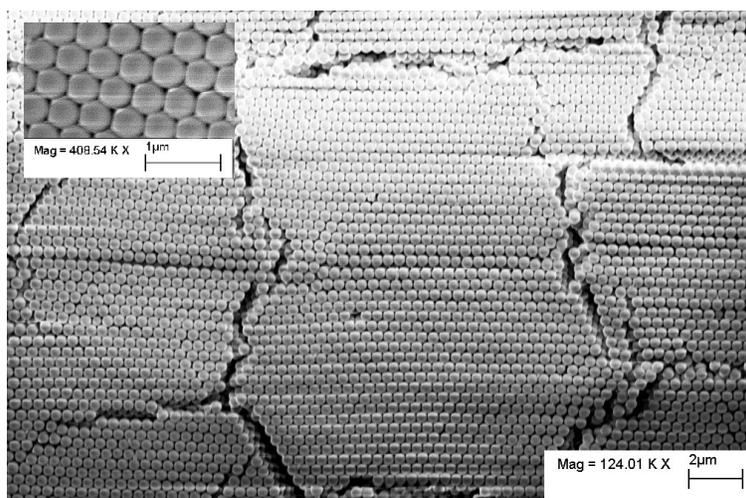
PCs via Self-Assembly

Success of getting a uniform photonic crystal very much depends on the successful self-assembly of templates in FCC arrangement, which in turn, depends solely on the monodispersity of the

silica spheres. Various methods were tried to synthesize monodisperse spheres with partial success. The two primary methods of self-assembly utilized were room-temperature crystallization [23] and electrophoresis [24]. The electrophoretic method is faster than crystallization and produces uniform crystal deposition. Concentrations of 1%, 0.5%, and 0.33% v/v ethanolic suspension were used. The use of higher concentrations led to thicker deposits, but did not affect the uniformity. The spheres were deposited on ITO- glass and silicon-ITO electrodes.

Samples made via electrophoretic deposition tended to dislodge from the substrate easily making it difficult to perform infiltration. Although crystallization is quite slow, it produces stable and uniform crystal deposition, which is better suited for infiltration. The assembly is heated in an oven at 700°C by a 5°C ramp, held at 700°C for four hours and cooled to room temperature to make it robust. Almost all the samples cracked during this process and can be seen in Figure 3.

Figure 3: SEM Image of 480nm Spheres Deposited via Crystallization



Infiltration of Templates

Low Pressure Chemical Vapor Deposition (LPCVD) has been shown to infiltrate silicon all the way to the substrate [25]. Since no Chemical Vapor Deposition facilities are available at MSFC, we tried to use:

- a. in *situ* chemical reactions
- b. sputtering for infiltration.

The possibility of using Physical Vapor Transport (PVT) is being explored.

a. in *situ* Chemical Reactions

Our preliminary trials were concentrated in trying to do in situ precipitations of gold, silver molybdenum and tungsten and were carried out by the general procedure as described below:

A drop of reactant A is placed on the crystals, kept covered for a few hours to ensure infiltration.

The excess A is wicked off; a drop of reactant B is placed to infiltrate and react over a few hours. The excess B is wicked off; a drop of water is placed briefly and wicked off. The crystals were allowed to dry.

One of the major problems encountered by us was the crystals with Si-ITO substrate tend to lift off completely in aqueous solutions; ethanolic solutions, on the other hand do not stay put and spreads immediately and evaporates away before it can infiltrate well into the structure. The reactions used for the precipitation of the metals are tried in vitro to establish the right conditions and to confirm the reduction to Zero oxidation state. X-ray fluorescence spectroscopy of the products from these last three reactions confirm the reduction proceeding to the metal level (Figures 4-6)

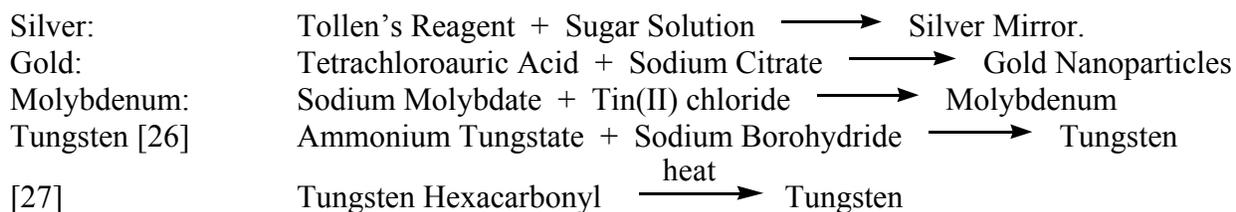


Figure 4: X-Ray Fluorescence Spectroscopy of Molybdenum

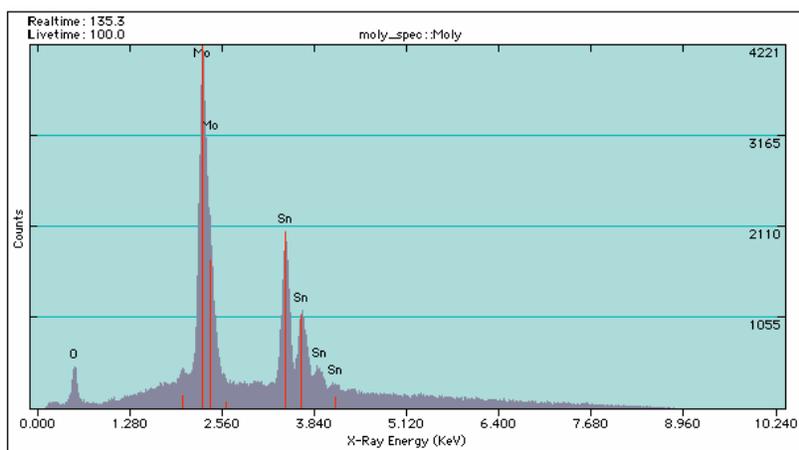


Figure 5: X-Ray Fluorescence Spectroscopy of Tungsten

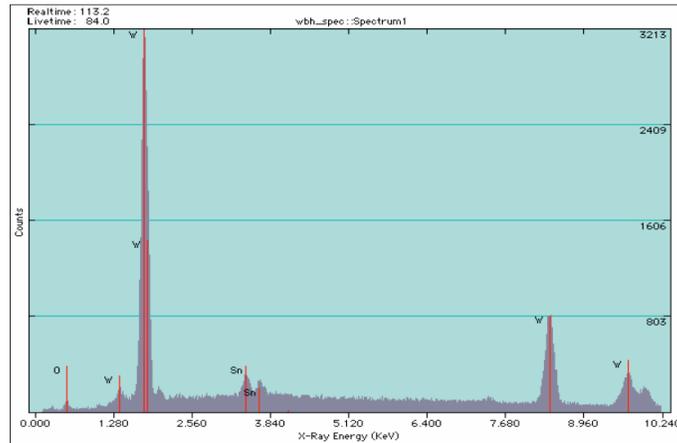
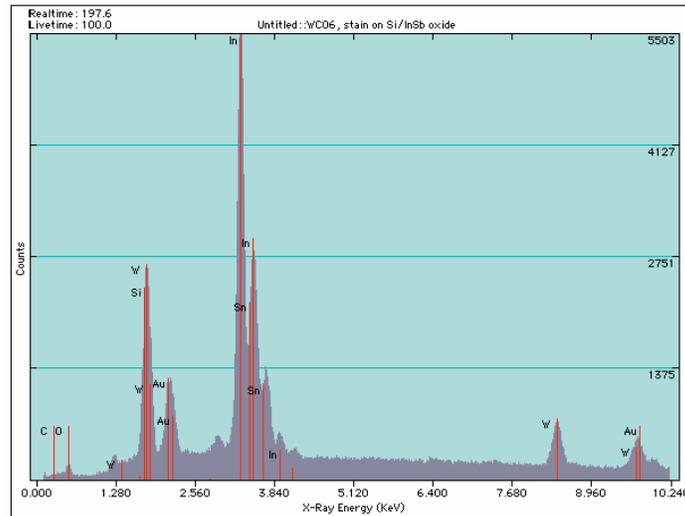
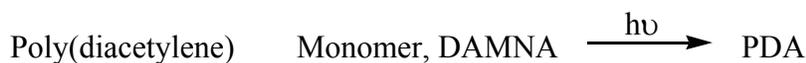


Figure 6: X-Ray of Tungsten From the Decomposition of $W-(CO)_6$



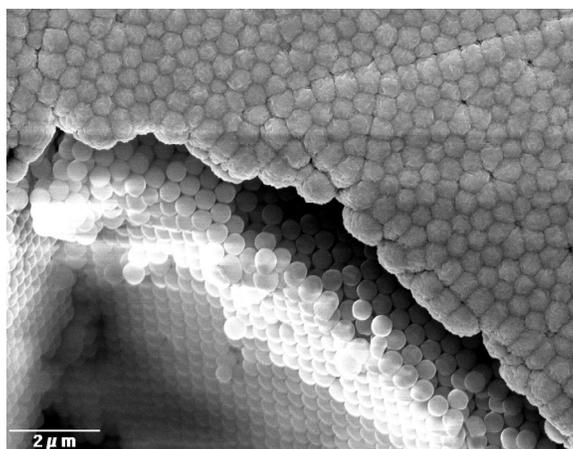
In situ polymerization shown below was also attempted:



b. Sputtering

The infiltration of silicon into the interstitial spaces was tried by sputtering with tungsten target. The tungsten coating was peeling off from the substrate and seems to hold a little better where on the crystal. Analysis of these samples was done using SEM to see whether tungsten penetrated all the interstitial sites. As Figure 7 clearly shows the tungsten just crystallizes on the first row of spheres, as expected. This may be a good way to make 1-D PCs.

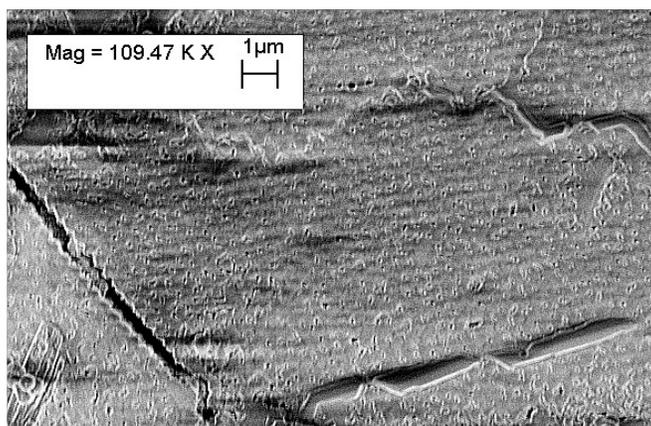
Figure 7: 480nm Spheres with Top Layer of Tungsten via Sputtering



Results from Infiltration

Preliminary results indicate that silver grains are successfully infiltrated and we believe that the same is true of gold infiltration also. The infiltration of Molybdenum went very smooth with high efficiency as Figure 8 shows.

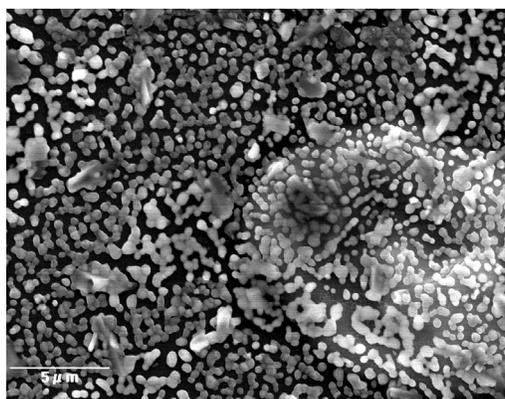
Figure 8: Sample Infiltrated by Molybdenum



Sodium borohydride reduction of ammonium tungstate is very fast at ambient temperature; however the tungsten reduction reaction proceeded via famous Tungsten blue in acidic medium and the evolution of gaseous hydrogen destroys the assembly. Non-destructive reduction of solid tungstate with glycerol proceeds at 170° but seems extremely slow with aqueous tungstate.

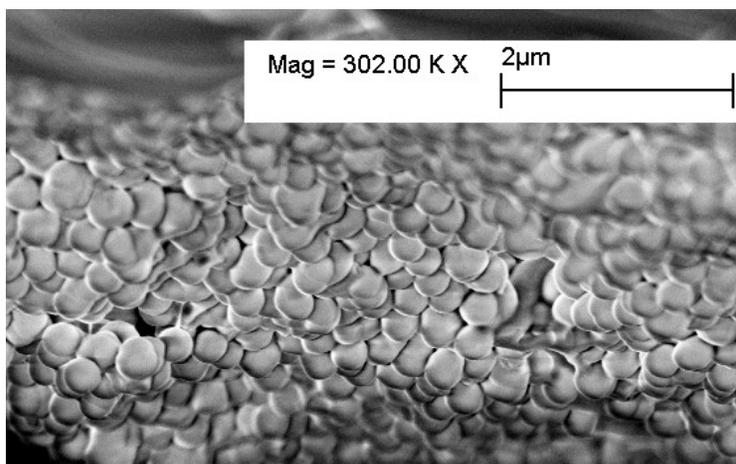
Another more direct route is by the thermal decomposition of tungsten hexacarbonyl, which as Figure 9 shows produces Tungsten at 700° C. We are exploring a very good solvent to dissolve hexacarbonyl for effective infiltration.

Figure 9: Tungsten From the Decomposition of $W-(CO)_6$



The attempts to do *in situ* photochemical polymerization of diacetylene monomer, DAMNA failed. 7 hours of irradiation was unable to give the desired result which suggests that the rate of polymerization is either too low or it does not occur at all. This hurdle was overcome by infiltrating the polymer solution, instead of the monomer. Preliminary results indicate that the polymer does infiltrate through the voids, given enough time (Figure 10). The polymer used in this trial was mixed with 10% of Poly (hydroxymethyl methacrylate) to decrease the brittle nature of the Poly (diacetylene), PDA.

Figure 10: Sample Infiltrated by PDA



Removal of Template from Molybdenum Opal

A drop of 1% HF was added over the crystal and allowed to remain for 20 min. It was noticed that after etching, the ITO coating is also etched off the glass substrate. The SEM analysis is yet to be done on the sample to see the success of the etching process to produce Mo inverse opals.

Future Efforts

The project is still in progress. Our future efforts need to be directed in the following areas:

- To standardize synthetic efforts to make monodisperse micron size spheres
- To make the electrophoretic assembly stick to the substrate better
- To refine *in situ* infiltration techniques
- To explore PVT and LPCVD for infiltration

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